THE MECHANISM OF THE ADDITION AND REMOVAL OF Br_2 IN A CARBON FIBER

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Introduction

In general, the behavior of carbon fibers depends on the source material, the pyrolysis program (temperature, time, and environment), and on special chemical post-treatments. For example, a commercial fiber can be designated as a low temperature (1200-1500°C), a medium (2000-2500°C), or a high temperature (above 3000°C) product. This paper is concerned with the interaction of bromine with some carbon fibers and the results are compared with those reported for the intercalation of bromine by crystalline graphites.

Materials

The fibers were selected from commercial sources using both PAN and pitch as precursors. F-5 is a Courtauld HM PAN fiber. F-46 is a Union Carbide carbon fiber, Type P, on which the finish, normally present, was removed by heating at 500°C in a helium flow. F-44 and F-54 are pitch-base fibers (Union Carbide) which had been heated above 3000°C. P-35 and P-36 were obtained as the residues from an air-bromine treatment of F-54 (45 hours at 20°C). Spec C SP-1 were flakes of purified natural graphite (100 μm) from National Carbon Co.

Experimental

The bromine adsorption and desorption isotherms (20°C, P_o = 177 torr) were determined on 100 mg samples in an all glass, recording vacuum balance (1). The x-ray diffraction results were determined by Carl Vold of the NRL Material Sciences Division using a Phillips Vertical Diffractometer (Cu source). The emission of bromine with temperature programming was determined by J. B. Romans of the NRL Surface Chemistry Branch using a modified microcoulombmeter (Mast Instrument Co.). The calibration was made with dry air saturated with a halogen of known vapor pressure.

Results

The bromine isotherms in Figure 1 for F-54 were first taken to saturation and back to zero pressure (points X for I and O for II). After the return to zero pressures, isotherm III (points +) and isotherm IV (points ⊕) were obtained without the pronounced threshold pressures of isotherms I and II. The three bromine isotherms in Figure 2 were not taken to saturation, but were returned to zero pressure from different positions of adsorption. No intercalation of Br_2 was found in F-46, even at saturation; also no emission of Br_2 was observed in the thermal cycling to 550°C of this fiber.

The 002 separations of an original fiber and the same fiber after bromine treatments are given in Table 1. The values are also given for the average dimension of the diffracting domain, the interpretation of which is given in Discussion.

The emission of bromine from P-36 is shown in Figure 3 for two complete heating cycles to 530°C using the same sample. The bromine contents of the fibers were determined by an activation analysis based on irradiation in a Linac Reactor using 40 MeV. Similar behavior was reported earlier for crystalline graphite(2).

Discussion

It is instructive to compare the 20°C isotherms of Br_2 on natural graphite, Spec C SP-1 (3) and on the highly graphitized F-54 carbon fiber.

1. Threshold Pressure, P_t

In the 100 μm flakes of natural graphite P_t is 15-20 torr. In F-54, diameter 18 μm, the value of P_t is 60 torr for the initial exposure to Br_2, but this drops to 10 torr after one cycle of saturation and back to zero pressure, Figure 1. This resembles the behavior of a 2200°C pyrolytic graphite PG1 (4) where P_t was initially 95 torr for a 7 mm thick sample. After one cycle to saturation and back to zero, the sample had split into thin flakes for which P_t was 60 torr. In the case of the fiber F-54, this same behavior would be expected if the graphite domains in the original fiber were interlocked or imbedded in a matrix. The resultant stress raises P_t to 60 torr above which intercalation and expansion occur.

The x-ray diffraction results in Table 1 agree with a model of interlocking crystallites.

Table 1: (002) Separation Before and After Bromine

	(002)	Diameter Diffracting Domain
F-44	3.371	670 Å
P-35	3.392	730
F-54	3.375	790
P-35	3.396	840
P-35 (500°C)	3.389	820

The average dimension of the diffracting domain is 770Å and in the cross-section of the fiber (18 μm diameter) there are 5×10^4 domains. Thus, each carbon fiber can be viewed as a carbon composite. The intercalation of Br_2 and expansion of each domain cracks the matrix in a great variety of places along and around the fiber and to different degrees. Because the carbon layers are mostly parallel to the fiber length, the cracks should also be parallel to the length. In fact, this can be seen in the SEM for PAN fibers (F-5) intercalated with $AlCl_3$. It was noted that the crack was longitudinal and not all the way through the fiber. Now, when the pressure of Br_2 in F-54 is lowered to zero, most of the Br_2 leaves the graphitized regions which collapse and allow the cracks to close so that the fiber approaches its original cross-sectional shape. When the Br_2 pressure is now raised again, the graphitized regions are again intercalated but at a lower P_t (10 torr) because the fiber is now under much less stress than the original fiber. This change is also shown by the rates of intercalation. Thus, in the initial exposure, the rate is very slow in the first 10 torr above P_t; beyond that and during the second intercalation, the rate is much faster.

Saunders, Ubbelohde and Young (5) showed that the application of pressure decreased the amount of Br_2 intercalated in graphite. The relief of an internal stress should behave in the reverse manner.

Finally, it is of interest that for the fiber F-46 the P_t was so high that even in saturated Br_2 vapor at 20°C there was almost no weight increase. This fiber had not been heat treated at as high a temperature as F-54, and it has been shown before that this will raise P_t for an electron accepting reactant such as Br_2. The intercalation pressure for the F-46 fiber may be above saturation pressure.

2. Composition near Saturation

The composition is best considered just below saturation so that condensation in the inter-fiber or inter-flake regions is not a factor (1). At 20°C, saturation pressure is 175 torr so that 160 torr is suitable. For the natural flakes in Spec C - SP1 the amount is
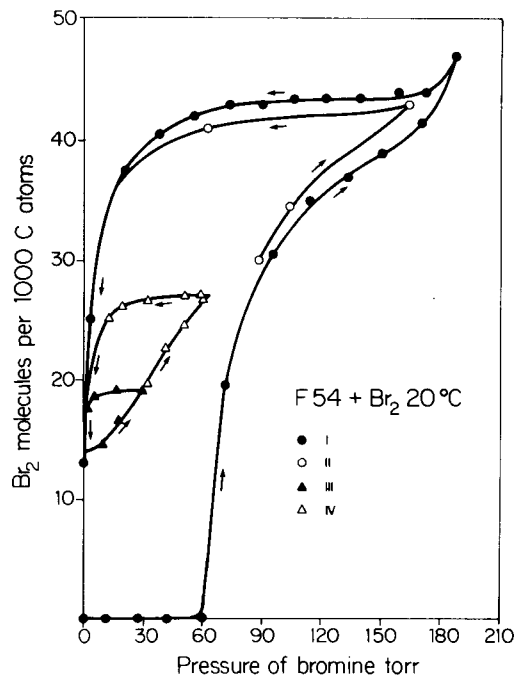

Figure 1: Intercalation adsorption and desorption isotherms (I, II original; III, IV after pumping).

$10^3 Br_2/C = 60$ or $C_{17}Br_2$. For the F-54 fiber it is 48 or $C_{21}Br_2$. This lower Br_2 content could well be the result of the presence of non-graphitized regions - the matrix referred to above - in which the intercalation of Br_2 does not take place.

3. Residue "Compound"

In the carbon fiber F-54, the residual Br_2 at zero pressure amounts to 14 moles per 1000 moles carbon. This is about three times the amount left in the 100 μm flakes of Spec C - SP1. Since the graphite crystallites in F-54 are about 7.7 nm across, one would expect a much smaller amount of residual Br_2 in such small crystals. One possible explanation is that when the fiber first cracked open, some of the internal porosity became exposed to Br_2 and filled with liquid as the pressure increased. On pressure reduction this region emptied at lower pressures than for filling and not completely because the closing of the cracks sealed them off. Specifically, the total volume of these pores for a fiber of density 1.6 gm cm^{-3} might be 0.6 cm^3 gm^{-1} and, if filled with liquid Br_2 would contribute 43 moles of Br_2 per 1000 moles carbon. This is the observed total amount near saturation. Much of this must be intercalated to account for the cracking of the fiber. An unknown, remaining amount is in the available pores and,